

Synthesis and reactivity of palladium cluster compounds¹

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Abstract

The synthesis, characterisation and reactions of a new group of palladium clusters are discussed. When $[\text{Pd}_2(\text{dba})_3]$ (dba = dibenzylideneacetone) and PBU_3^t react in the presence of organic halides CRCl_3 (R = H, F) the novel methylidyne cluster compounds $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Cl})_3(\text{PBU}_3^t)_4]$ are obtained. These are the first examples of μ_3 -alkylidyne palladium compounds. They undergo substitution reactions with LiBr and with phosphines (e.g. PCy_3) to yield the cluster compounds $[\text{Pd}_3(\mu_3\text{-CR})(\mu\text{-Br})_3(\text{PBU}_3^t)_4]$ with H_2 leads to cluster fragmentation and the capping $\mu_3\text{-CF}$ fragment is converted to CFH_3 . The reaction is an important component of a potential catalytic cycle for the conversion of CFCl_3 to CFH_3 . This reaction is particularly relevant because of the current interest in finding efficient routes to convert CFCs to HFCs. The reactions between $[\text{Pd}_2(\text{dba})_3]$, PBU_3^t and the organic halides CHX_3 (X = Br, I) have also been studied and the dimers $[\text{Pd}_2(\mu\text{-X})_2(\text{PBU}_3^t)_2]$ have been obtained. Their reactions with CNXyl , H_2 , CO, $[\text{Co}_2(\text{CO})_8]$ and $[\text{Fe}_2(\text{CO})_9]$ have been studied and some interesting products have been obtained. The reactions with $[\text{Co}_2(\text{CO})_8]$ have led to the novel heteronuclear clusters $[\text{CoPd}_3(\mu_3\text{-X})(\mu\text{-CO})_3(\text{CO})_2(\text{PBU}_3^t)_3]$ (X = Cl, Br, I). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Palladium clusters; Cluster fragmentation; Heteronuclear clusters

1. Introduction

Metal cluster chemistry is a field that has developed considerably during the last three decades [1,2]. Initially, cluster compounds were prepared by chance, but more recently well defined synthetic strategies have been developed. With the advent of advanced characterisation techniques (principally X-ray diffractometry and NMR spectroscopy) their structures have been elucidated more quickly and their reactivities have been studied more extensively. It has long been suggested that metal cluster compounds represent a *bridge* between the bulk metal and mono-metallic species [3]. As such, the study of their reactions may illuminate the reactions that occur on metal surfaces [4]. The study of molecular cluster com-

pounds has assisted the characterisation of organic fragments bound to metal surfaces. In addition, it is anticipated that some metal cluster compounds may prove to be good catalysts in their own right [5].

Coordination and organometallic compounds of palladium have been used as catalysts for a wide variety of organic transformations [6]. Therefore, it comes as something of a surprise that palladium cluster chemistry is less well developed than that of other metals. There have been some previous reviews on palladium cluster chemistry [7–9] so a detailed account of previous work in the area will not be given here. Instead, we will present some of the most recent advances in the synthesis and reactivity of halogen-containing palladium cluster compounds.

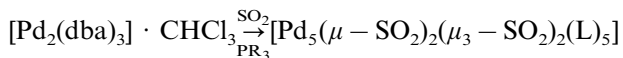
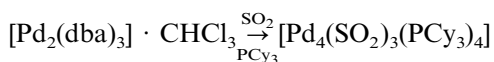
2. $[\text{Pd}_2(\text{dba})_3]$ in the synthesis of cluster compounds

Two general methods have been developed for the synthesis of palladium cluster compounds [7]. One of

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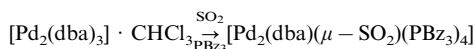
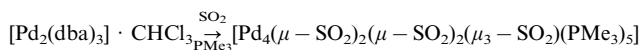
them is based on the aggregation of mono-metallic palladium fragments. These fragments may be produced by the reduction of higher oxidation state complexes or by using preformed zero-oxidation state palladium compounds with labile ligands. $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ (dba = dibenzylideneacetone) has proved to be a particularly flexible precursor. Several systems have been studied in which $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ is allowed to react with 1 mol equivalent of phosphine per palladium under an atmosphere of small π -acid molecules such as CO and SO_2 . The nuclearity of the clusters obtained from these reactions depends to a large extent on the steric properties of the phosphine. This research group has systematically studied the reactions between $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ and SO_2 with a range of phosphines. A tetranuclear cluster was obtained with PCy_3 , which has a large cone angle, while penta-palladium clusters were synthesised with PPh_3 , PMePh_2 , PPh_2Me , AsPh_3 and $\text{P}(m\text{-C}_6\text{H}_4\text{OMe})_3$ [10,11].



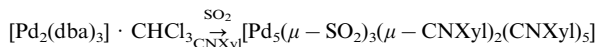
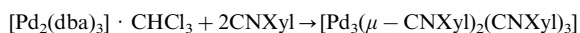
L = PPh_3 , PMePh_2 , PMe_2Ph , AsPh_3 , $\text{P}(m\text{-C}_6\text{H}_4\text{OMe})_3$

In the presence of PMe_3 a tetra-palladium cluster with a butterfly arrangement was obtained suggesting that steric effects are not the only influence on cluster geometry. In general the dba ligand serves only as a good leaving group, but recently, the crystal structure of the product obtained from the reaction between $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$, SO_2 and PBz_3 , has revealed that a

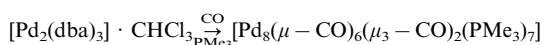
bridging dba molecule is retained in the binuclear product [12].



Other workers have reported the use of $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ in the synthesis of palladium-isocyanide clusters according to the following equations [13,14]:

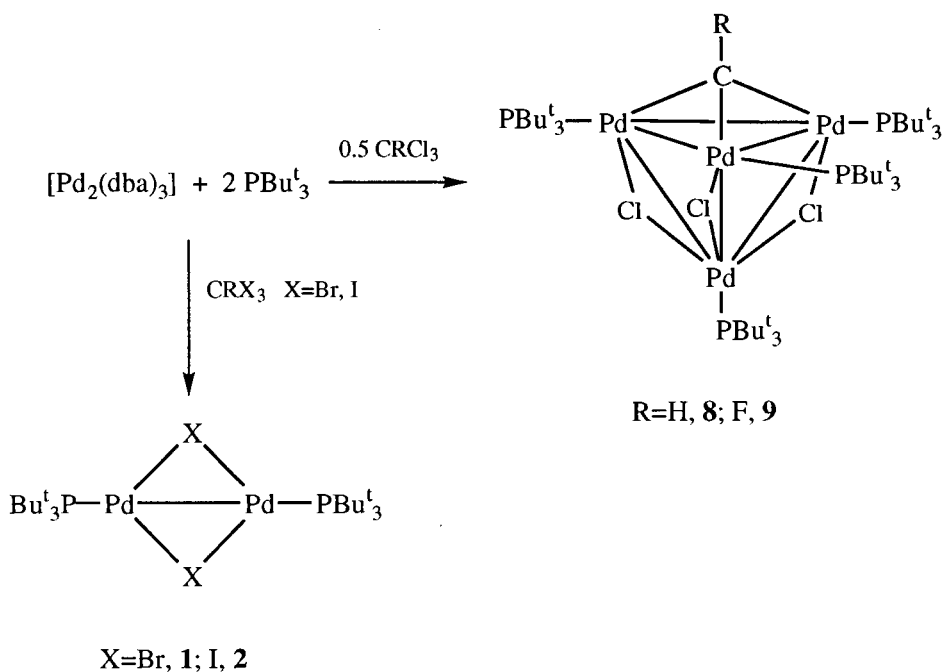


Bochmann and co-workers have reported that $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ readily reacts with CO in the presence of PMe_3 to give an octanuclear cluster [15]:

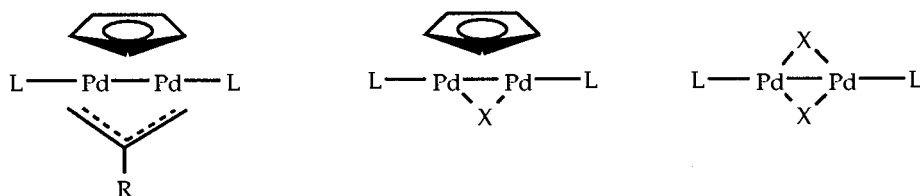


3. Participation of organic halides in palladium cluster reactions

In the reactions described above the solvent does not participate significantly in the cluster aggregation reaction, however when chlorinated solvents were used some interesting new products were obtained. Specifically $[\text{Pd}_2(\text{dba})_3] \cdot \text{C}_6\text{H}_6/2\text{PBu}_3^t$ reacts with organic halides giving either cluster compounds in which the organic fragments are incorporated into the cluster or some unusual palladium(I) dimers (see Scheme 1)



Scheme 1. Reactions between $[\text{Pd}_2(\text{dba})_3]$, PBu_3^t and organic halides.



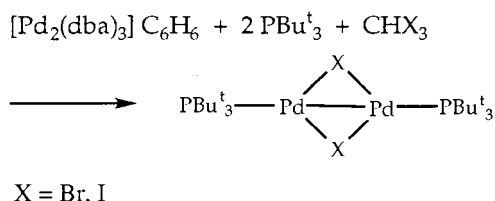
Scheme 2. Some examples of palladium(I) dimers.

[16,17]. The main purpose of this review is to discuss these polynuclear palladium compounds and their chemistry.

3.1. Chemistry of the dimers $[Pd_2(\mu-X)_2(PBu_3)_2]$ ($X = Br, I$)

Palladium(I) dimers containing bridging cyclopentadienyl and allyl ligands (see Scheme 2) have been known for some time and their relevance to organic coupling reactions catalysed by palladium compounds has been widely discussed [18,19]. However, the corresponding simple halogen bridged dimers **1** and **2** have not been reported until recently [20].

The dimers **1** and **2** are obtained as either green or purple crystalline compounds when $[Pd_2(dba)_3] \cdot C_6H_6$, dissolved in toluene, is allowed to react with two equivalents of PBu_3^t and one equivalent of CHX_3 ($X = Br, I$):

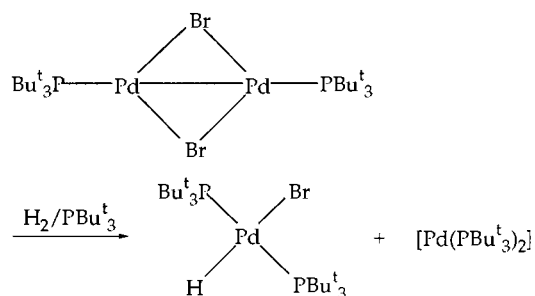


The molecular structure of $[Pd_2(\mu-Br)_2(PBu_3^t)_2]$ has demonstrated that these compounds have effectively C_{2h} symmetry with a Pd–Pd bond distance of 2.621(2) Å [20] (see Table 1). The majority of the Pd(I) dimers which have been previously characterised are derived from square-planar fragments, whereas these compounds and those previously reported by Kurosawa [22,23] and Felkin [24] have trigonal coordination geometries if the metal–metal bond is excluded.

The reactions of $[Pd_2(\mu-X)_2(PBu_3^t)_2]$ ($X = Br, I$) which have been investigated to date are summarised in Scheme 3 (D.M.P. Mingos, R. Vilar, unpublished results). These dimers show a range of different reactions. In some cases, aggregation to higher nuclearity compounds is observed whilst in others simple fragmentation to mononuclear compounds occurs. Only in the reactions of **1** and **2** with isocyanides are the dimeric skeletons of the original compounds retained.

3.1.1. Reaction with H_2

Palladium and platinum hydrido compounds have been implicated in several catalytic reactions [25]. Very few dimers or clusters of palladium with hydrido groups coordinated to the metal core have been reported, however [26]. When H_2 is bubbled through a solution of $[Pd_2(\mu-Br)_2(PBu_3^t)_2]$ in toluene the product obtained is *trans*- $[Pd(H)(Br)(PBu_3^t)_2]$ and palladium metal. When the same reaction was repeated in the presence of two equivalents of PBu_3^t palladium metal was no longer formed since it was scavenged by the phosphine as $[Pd(PBu_3^t)_2]$.



In contrast when H_2 is bubbled through a solution of $[Pd_2(\mu-I)_2(PBu_3^t)_2]$ in toluene, no reaction was observed.

3.1.2. Reaction with CO

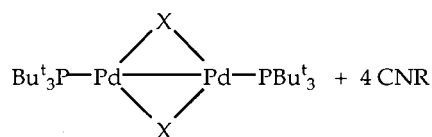
The addition of ligands to a pre-formed cluster can lead to a simple substitution reaction. However, sometimes the process is more complicated and cluster aggregation occurs. It has been previously observed that the reaction of some palladium clusters with CO leads to higher nuclearity compounds [27]. When CO was bubbled through a solution of $[Pd_2(\mu-Br)_2(PBu_3^t)_2]$ in toluene an immediate colour change from green to dark orange was observed. $^{31}P\{-^1H\}$ NMR spectroscopy showed the formation of two different products. Careful recrystallisation led to the separation of two products which were characterised as $[Pd_4(\mu-Br)_3(\mu-CO)_2(Bu_2PCMe_2CH_2)(PBu_3^t)_2]$ (**3**) and $[Pd_6(\mu-Br)_4(\mu-CO)_4(PBu_3^t)_4]$ (**4**) (see Scheme 4). These compounds both contain the triangular $[Pd_3(\mu-Br)(\mu-CO)_2(PBu_3^t)_2Br]$ fragment, but in the latter case the structure is based on a dimer of these fragments linked by bromide bridges while the former has it linked to a cyclometallated palladium monomer.

Interestingly cluster **3** has also been obtained as the major product of the reaction of $[\text{Pd}_4(\text{OAc})_4(\text{PBu}_3)_4]$ with PBu_3 and CBr_4 .

The dimer $[\text{Pd}_2(\mu\text{-I})_2(\text{PBu}_3)_2]$ also reacts with CO, however the reaction is reversible. From this reaction, it has been possible to isolate and spectroscopically characterise the compound $[\text{Pd}_6(\mu\text{-CO})_4(\mu\text{-I})_4(\text{PBu}_3)_4]$ (**5**).

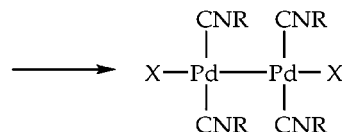
3.1.3. Reaction with CNXyl

Isocyanides behave in many respects like CO and can exhibit terminal or bridging coordination modes. The reactions between $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$ ($\text{X} = \text{Br}, \text{I}$) and CNXyl have resulted in the formation of the dimers $[\text{Pd}_2\text{X}_2(\text{CNXyl})_4]$ ($\text{X} = \text{Br}, \text{6}; \text{I}, \text{7}$).



$\text{X} = \text{Br}, \text{I}$

$\text{R} = \text{Xyl}$



$\text{X} = \text{Br}, \text{6}; \text{I}, \text{7}$

This type of compounds have been previously prepared from $[\text{Pd}(\text{dba})_2]$, $[\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$ and CNR by Retting and Maitlis [28]. The X-Ray crystal structures of $[\text{Pd}_2\text{I}_2(\text{CNMe})_4]$ and $[\text{Pd}_2\text{Cl}_2(\text{CNBu}^t)_4]$ have also been reported by Yamamoto [29] and Balch respectively [30] and are based in two square-planar palladium units sharing a metal–metal bond.

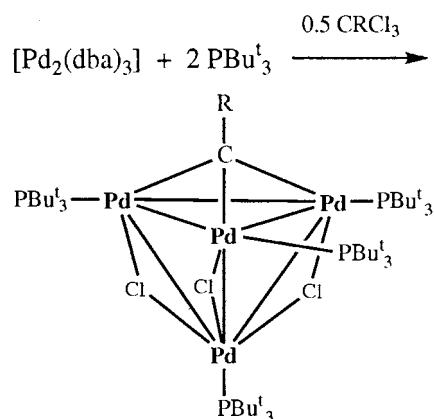
3.2. Chemistry of the tetrapalladium clusters

$[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-X})_3(\text{PBu}_3)_4]$

The coordination of small molecules or fragments of molecules on crystallographically characterised metal surfaces has been extensively studied because of their possible catalytic implications [1]. Cluster chemistry has

proved particularly useful for identifying the spectroscopic signatures of the organic fragments [2]. The methylidyne ligand is such a fragment and its cluster chemistry has been extensively studied for cobalt [31], iron [32] and ruthenium [33]. Homometallic alkyldiene clusters of the metals in the triad nickel, palladium, platinum have been reported only for nickel [34]. Heterometallic alkyldiene clusters of nickel have been prepared by Vahrenkamp and coworkers [35] and of platinum by Stone and his coworkers [36]. The ethyldiene ligand has been identified spectroscopically on clean Pt(111) crystal surfaces [37] and has been implicated as an intermediate in heterogeneous catalytic processes involving the hydrogenation of CO and C_2H_2 [38,39]. The first examples of triply bridging alkyldiene clusters of palladium have been recently described by us. The relevance of this to surface studies and the possible catalytic implications of this type of compound make it an interesting system for study. The syntheses, characterisation and reactivity of $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ (**8**) and $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ (**9**) are described below.

The reaction between $[\text{Pd}_2(\text{dba})_3] \cdot \text{C}_6\text{H}_6$, PBu_3 and CRCl_3 ($\text{R} = \text{H}, \text{F}$) led to the syntheses of the first two $\mu_3\text{-CR}$ Pd methylidyne clusters $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ ($\text{R} = \text{H}, \text{F}$) [16,17].

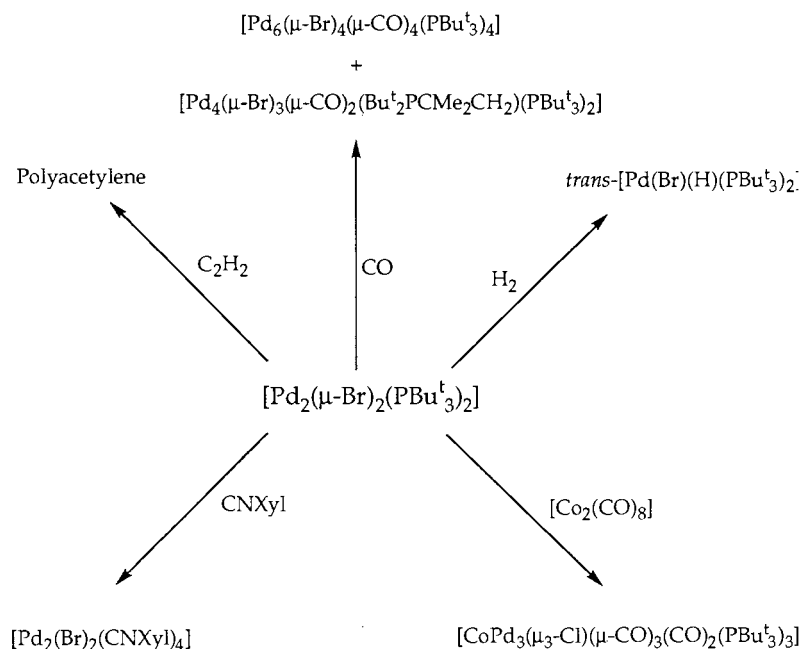


One of these clusters (when $\text{R} = \text{H}$) has been structurally characterised and the molecular structure showed that it is a tetrahedral cluster with a face capping methylidyne ligand [16]. Besides the μ_3 -methylidyne ligand the chlorine atoms of the CHCl_3 molecule

Table 1

Palladium–palladium distances and geometries for selected palladium cluster compounds

Compound	Geometry	Pd–Pd (Å)	Ref.
$[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$	Tetrahedral	2.989(1), 2.743(1), 2.948(1), 3.143(1)	[16]
$[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Br})_3(\text{PBu}_3)_4]$	Tetrahedral	3.112(2), 2.727(2), 2.729(2), 3.097(2)	[17]
$[\text{Pd}_2(\mu\text{-Br})_2(\text{PBu}_3)_2]$	Linear	2.628(2)	[20]
$[\text{CoPd}_3(\mu_3\text{-Cl})(\mu\text{-CO})_3(\text{CO})_2(\text{PBu}_3)_5]$	Butterfly	2.903(1), 2.952(1), 3.324(8)	[21]
$[\text{Pd}_6(\mu\text{-Br})_4(\mu\text{-CO})_4(\text{PBu}_3)_4]$	Bridged triangles	2.893(2), 2.686(2), 2.750(2), 3.405(3)	[21]

Scheme 3. Reactions of $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$ investigated to date.

are retained within the cluster and bridge three of its edges giving an effective C_{3v} symmetry to the metal cluster skeleton. The polyhedral electron count in the methylidyne cluster is 60, which is the closed shell requirement for a tetrahedral cluster according to the Polyhedral Skeletal Electron-Pair Theory [40].

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of these clusters is very characteristic and represents an important feature for the study of their reactions (see Table 2). $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ showed a quartet at 100.2 ppm and a doublet at 74.0 ppm ($^3J(\text{PP}) = 132.2$ Hz) which is consistent with a C_{3v} structure in solution. The methylidyne ^1H NMR resonance is observed as a doublet of quartets at 11.6 ppm which is in the range previously reported for μ_3 -methylidyne complexes [32]. In the IR spectrum the CH stretching frequency is obscured by ligand vibrations but $\nu(\text{C-D})$ for the corresponding compound prepared from CDCl_3 is observed at 2162 cm^{-1} .

Although other μ_3 -methylidyne cluster compounds have previously been synthesised [31] from CRCl_3 this cluster is unique in retaining all the atoms of the CRCl_3 molecule within the cluster. The final product appears to structurally document the effective chemisorption of a CRCl_3 molecule by a tetrahedral metal cluster with the simultaneous breaking of three C–Cl bonds, though this is unlikely to be an accurate reflection of the actual mechanism. The cluster aggregation is more likely to proceed via a series of oxidative–addition reactions.

The reactions leading to the methylidyne clusters $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ ($\text{R} = \text{H}, \text{F}$) are very sensitive to the electronic and steric factors of the reactants.

Several different phosphines and organic halides have been studied in order to develop this into a more general route to methylidyne clusters. However, PBu_3 is currently the only phosphine that gives just the appropriate electronic and steric factors to lead to the formation of the alkylidyne clusters and CHCl_3 and CFCl_3 are the only two organic halides that have resulted in capping methylidyne ligands. As has already been discussed in the previous section, organic bromides and iodides (i.e. CHBr_3 , CHI_3 and CBr_4) give the dimers $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$ instead of the methylidyne clusters.

The capping CR groups in $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ ($\text{R} = \text{H}, \text{F}$) make them very interesting from the reactivity point of view. These clusters have several potential reaction sites. The bridging halogens and the terminal phosphines are suitable sites for substitution reactions, but the most interesting group in these clusters is the $\mu_3\text{-CR}$ capping ligand. This can be regarded as an *activated* organic fragment on a metal face since it resembles the intermediate species proposed in certain catalytic processes on metal surfaces. In the following sections, some of the reactions of these clusters will be discussed.

3.2.1. Halogen substitution

The methylidyne clusters $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ ($\text{R} = \text{H}, \text{F}$) were allowed to react with three equivalents of LiBr in acetone at room temperature for 4 h and the new fully substituted clusters $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Br})_3(\text{PBu}_3)_4]$ ($\text{R} = \text{H}, \mathbf{10}$; $\text{F}, \mathbf{11}$) were obtained [41]. These compounds were identified in solution through $^{31}\text{P}\{-^1\text{H}\}$ NMR, and in one case ($\text{R} = \text{F}$) crystals suitable for X-Ray analysis were obtained from a benzene

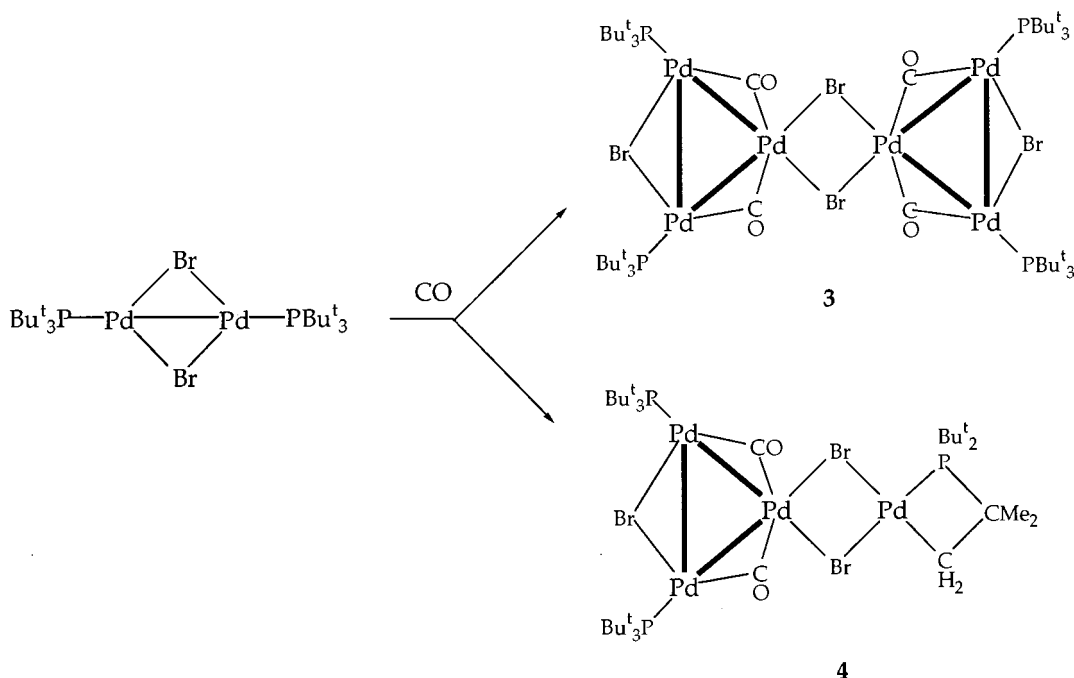
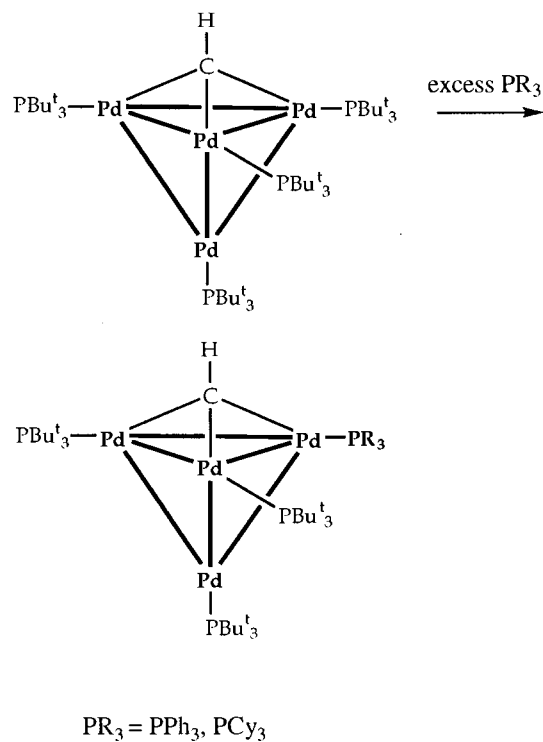
solution at 4°C overnight. The molecular structure of $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Br})_3(\text{PBu}_3)_4]$ confirmed that the tetrahedral metal core and the capping CF group of the original compound had been retained and the chlorine atoms had been substituted by bromine atoms [17]. As with the structure of the cluster $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$, this compound is sterically strained by the presence of the bridging groups and the bulky PBu_3 ligands. The Pd–Pd bonds cover a range of lengths from 2.727(2) to 3.123(2) Å (see Table 1).

Although the fully substituted clusters $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Br})_3(\text{PBu}_3)_4]$ (R = H, F) may be readily made using an excess of LiBr, during the study of the reactions between $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ and LiBr, the intermediate halide derivatives $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Br})(\mu\text{-Cl})_2(\text{PBu}_3)_4]$ and $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Br})_2(\mu\text{-Cl})(\text{PBu}_3)_4]$ shown in Scheme 5 have also been identified by $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy.

In $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Br})(\mu\text{-Cl})_2(\text{PBu}_3)_4]$ three different phosphine environments are observed in its $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum: a doublet of triplets at 101.6 ppm (corresponding to the apical PBu_3), a doublet of triplets at 78.9 ppm (corresponding to the PBu_3 neighbour to the bridging Br ligand) and a doublet of doublets at 72.2 ppm (assigned to the remaining two phosphines). For $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Br})_2(\mu\text{-Cl})(\text{PBu}_3)_4]$ a characteristic doublet of triplets at 105.5 ppm (corresponding to the apical PBu_3), a doublet of doublets at 77.3 ppm (corresponding to the PBu_3 neighbour to the only Cl) and a doublet of triplets at 71.2 ppm (assigned to the two remaining phosphines in the Pd triangle) were observed. The chemical shifts and coupling constants for all these compounds are summarised in Table 2.

3.2.2. Phosphine substitution

The second potential reaction site on the cluster involves the phosphines. When the methylidyne compound $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ was allowed to react with four equivalents of either PPh_3 or PCy_3 only the monosubstituted products $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_3(\text{PPh}_3)]$ and $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_3(\text{PCy}_3)]$ were observed.



Scheme 4. Products of the reaction between $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$ and CO.

Table 2
 $^{31}\text{P}\{-^1\text{H}\}$ NMR data for selected palladium cluster compounds

Compound	δ (ppm)	Solvent	Ref
$[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$	100.2 (1P, q), 74.0 (3P, d) $J = 132.2$	$(\text{CD}_3)_2\text{CO}$	[16]
$[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Br})(\mu\text{-Cl})_2(\text{PBu}_3)_4]$	101.6(1P, d), 78.9(1P, dt), 72.2(2P, dd) $J = 139.0, 128.8, 20.3$	$(\text{CD}_3)_2\text{CO}$	[41]
$[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Br})_2(\mu\text{-Cl})(\text{PBu}_3)_4]$	105.5(P, dt), 77.3(2P, dd), 71.2(P, dt) $J = 139.0, 152.6, 23.7$	$(\text{CD}_3)_2\text{CO}$	[41]
$[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Br})_3(\text{PBu}_3)_4]$	108.3 (1P, q), 76.5 (3P, d) $J = 149.2$	$(\text{CD}_3)_2\text{CO}$	[41]
$[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$	103.4 (1P, dq), 68.6 (3P, dd) $J(\text{PP}) = 132.2, J(\text{PF}) = 39.7, 8.5$	C_6D_6	[17]
$[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Br})_3(\text{PBu}_3)_4]$	117.0(1P, dq), 70.5 (3P, dd) $J(\text{PP}) = 173.0, J(\text{PF}) = 40.1, 11.0$	C_6D_6	[17]
$[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_3(\text{PPh}_3)]$	98.5 (1P, dt), 76.5(2P, dd), $-2.0(1\text{P}, \text{dt}) J = 139.0, 125.6, 20.4$	$(\text{CD}_3)_2\text{CO}$	[41]
$[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_3(\text{PCy}_3)]$	97.1(1P, dt), 75.9(2P, dd), 26.7(1P, dt) $J = 139.0, 125.5, 17.0$	$(\text{CD}_3)_2\text{CO}$	[41]
$[\text{Pd}_2(\mu\text{-Br})_2(\text{PBu}_3)_2]$	87.0 (s)	$\text{C}_6\text{D}_6\text{CD}_3$	[20]
$[\text{Pd}_2(\mu\text{-I})_2(\text{PBu}_3)_2]$	102.9 (s)	$\text{C}_6\text{D}_6\text{CD}_3$	[20]
$[\text{CoPd}_3(\mu_3\text{-Cl})(\mu\text{-CO})_3(\text{CO})_2(\text{PBu}_3)_3]$	77.3 (s)	C_6D_6	[21]
$[\text{CoPd}_3(\mu_3\text{-Br})(\mu\text{-CO})_3(\text{CO})_2(\text{PBu}_3)_3]$	78.7 (s)	C_6D_6	[21]
$[\text{CoPd}_3(\mu_3\text{-I})(\mu\text{-CO})_3(\text{CO})_2(\text{PBu}_3)_3]$	82.3 (s)	C_6D_6	[21]
$[\text{Pd}_4(\mu\text{-Br})_4(\mu\text{-CO})_4(\text{PBu}_3)_4]$	87.0 (s)	C_6D_6	(D.M.P. Mingos, R. Vilar, unpublished results)

These compounds were characterised by their $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra (see Table 2). The spectroscopic data suggest that the phosphine that has undergone substitution is not the apical one but one of the three (equivalent) phosphines in the Pd triangle bonded to CH. This explains the complexity of the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra in which three different phosphine environments were identified. One of them is a doublet of triplets (at 98.5 ppm when PPh_3 was used and 97.1 ppm when PCy_3 was used) corresponding to the apical PBu_3 phosphine. The two equivalent PBu_3 gave a doublet of doublets (at 76.5 ppm when PPh_3 was used and at 75.9 when PCy_3 was used). Finally, the PPh_3 (in compound $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_3(\text{PPh}_3)]$) and PCy_3 (in compound $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_3(\text{PCy}_3)]$) resonances were found at -2.0 ppm and 26.7 ppm respectively showing a doublet of triplets (see Table 2).

In summary, the substitution reactions described above have shown some interesting and significant differences. For bromide the sequential replacement of all three chloride ligands is achieved. In contrast the phosphine substitution reaction results in the substitution of only one of the equatorial phosphines. The fact that one of the phosphines is more labile than the others is intriguing and suggests that $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ may participate in some interesting catalytic reactions.

Attempts to substitute the R group of the $\mu_3\text{-CR}$ fragment have been made but did not yield tractable products. The first attempt to remove the R group, involved reacting $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ with $[\text{Ph}_3\text{C}]^+[\text{BF}_4]^-$. This compound is known to remove H groups from organic compounds. The reaction was carried out at -80°C and it was warmed up to 0°C .

A colour change was observed below 0°C (from dark green to dark red). However, the new colour disappeared in seconds giving a pale orange solution. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum showed that the cluster-core structure was not retained. Two new signals appeared, one of them at -10.0 ppm suggesting the formation of cyclometallation products and a second singlet at 50.2 ppm that has not been identified. Presumably, what happens is that the Ph_3C^+ is abstracting the hydrogen of the $\mu_3\text{-CH}$ group but the carbocation formed is highly reactive. In order to try to stop the cluster fragmentation, the reaction was repeated in the presence of pyridine (to trap the carbocation by coordinate bond formation) but this was not successful either.

The second approach consisted of reacting $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ with Lewis acids. It is known that, for the iron fluoromethylidyne clusters, the fluorine atom of the $\mu_3\text{-CF}$ capping group can be extracted using strong Lewis acids such as AlX_3 or BX_3 ($\text{X} = \text{Cl}, \text{Br}$) [42]. The substituted clusters with a $\mu_3\text{-CX}$ ($\text{X} = \text{Cl}, \text{Br}$) capping group would be potentially more reactive. Unfortunately, these reactions resulted in cluster fragmentation.

When the milder, BrSiMe_3 reagent was allowed to react with $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ substitution of the chloride bridging ligands of the cluster was observed (the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum showed the signals for $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Br})_3(\text{PBu}_3)_4]$ and the mixed-halogen clusters $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Br})(\mu\text{-Cl})_2(\text{PBu}_3)_4]$ and $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Br})_2(\mu\text{-Cl})(\text{PBu}_3)_4]$). Even when an excess of BrSiMe_3 was added substitution of the fluoride group failed to occur. Similarly when ClSiMe_3 was allowed to react with $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ for several hours, no substitution of the

fluoride atom was observed. The $^{31}\text{P}\{-^1\text{H}\}$ NMR indicated cluster degradation and presence of cyclometalated products.

These reactions showed that the substitution reactions at the $\mu_3\text{-CR}$ group are possible, but do not lead to tractable products. The bridging halides in the cluster core, are probably more reactive towards Lewis acids and if they are removed the cluster breaks down.

3.2.3. Reactions with acetylenes

The most interesting reactive site on these clusters is the capping $\mu_3\text{-CR}$ group. The fact that the carbon atom is bonded to three metal centres changes significantly its electronic properties making it suitable for reaction with several organic substrates. It has previously been observed that methylidyne cobalt clusters react with acetylenes giving products in which the acetylenes have inserted in the C–M bond giving a bridging allyl group [43]. When acetylene was bubbled through a solution of $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ in toluene polyacetylene was formed and identified by IR, analyses and mass spectrometry. After filtration, it was observed that the solution kept the colour of the original compound. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of this solution showed that the cluster remained essentially intact. Similar results were observed with $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$. In order to see if the original $\mu_3\text{-CH}$ ligand of the cluster was displaced and incorporated in the polyacetylene, the same reaction was carried out using $[\text{Pd}_4(\mu_3\text{-CD})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$. However, no displacement of the

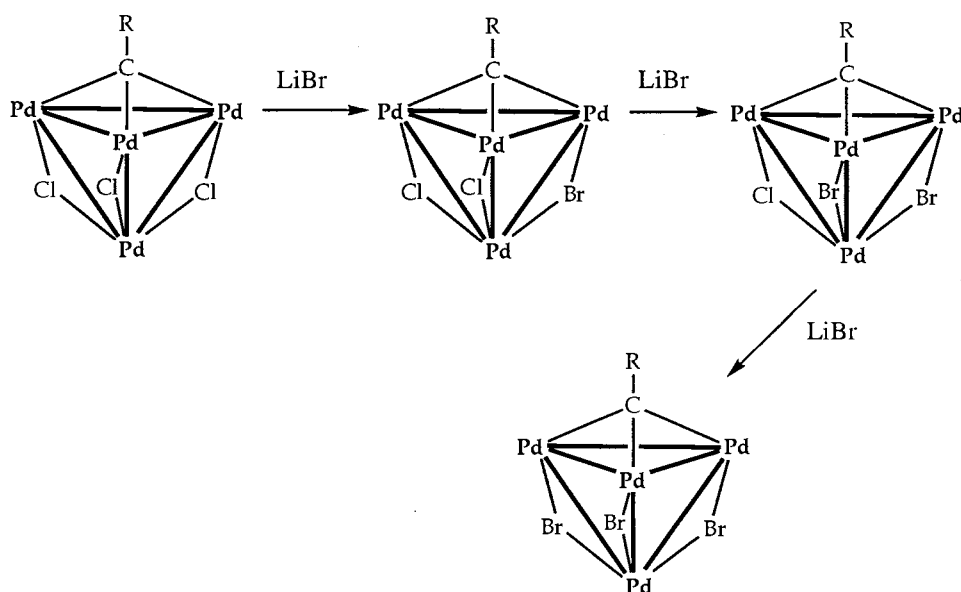
CD group in the cluster was observed. When $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ was used in this reaction, the displacement and substitution of the CF group by a CH group from the acetylene, was not observed either. This suggests that the capping ligand is not involved directly in this catalytic polymerisation reaction. It is possible that the initial steps of the polymerisation occur when a phosphine (probably the most labile one) is substituted by the incoming acetylene.

When $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ was treated with phenylacetylene for a period of 4 h, complete disintegration of the cluster was observed. This reaction was monitored using ^{31}P and ^1H NMR. After 4 h around 20 unrelated signals of different intensities were observed in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum. The cluster decomposed giving an enormous variety of compounds that could not be separated. Polyphenylacetylene was detected in the ^1H NMR spectrum.

In contrast, when $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ was treated with diphenylacetylene no reaction was observed. The cluster kept its structure without modification and no polymerisation of the acetylene was observed. These observations suggest that the polymerisation of acetylenes using $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ only occurs if there is a terminal (acidic) proton on the acetylene.

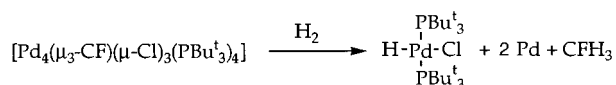
3.2.4. Reaction between $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ and H_2

When H_2 was bubbled for 15 min through a solution

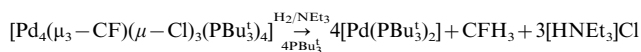


Scheme 5. Sequential substitution of Cl by Br in the methylidyne clusters (the phosphine groups have been omitted for clarity).

of $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3^t)_4]$ in toluene at room temperature and the reaction was left to stand for 2 h under a hydrogen atmosphere, the original green colour of the solution disappeared giving a dark precipitate (palladium black) and a clear solution [17]. After filtering the solution from the black palladium, the solvent was removed under reduced pressure and the remaining white solid recrystallised from hexane at 4°C. The colourless crystals were identified as the known compound *trans*- $[\text{PdHCl}(\text{PBu}_3^t)_2]$ on the basis of $^{31}\text{P}\text{-}\{^1\text{H}\}$ and ^1H NMR. A singlet at 82.4 ppm was observed in the $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR while a triplet at the characteristic Pd-H high-field region (-16.4 ppm) was detected in the ^1H NMR. CFH_3 was also detected as the sole organic product of the hydrogenation reaction. This results suggested that the following reaction has taken place:

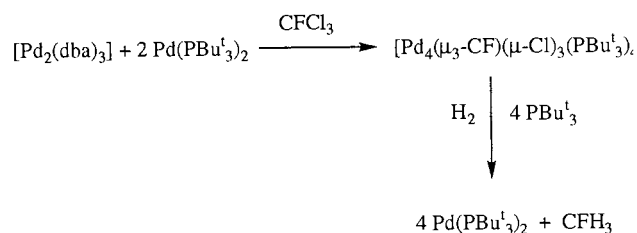


To prevent the formation of palladium black, four additional equivalents of PBu_3^t were added to the reaction mixture. Secondly an excess of NEt_3 was added. The amine encourages the heterolytic cleavage of H_2 forming $[\text{HNEt}_3]^+$. The following reaction then takes place at room temperature and without the formation of palladium metal:



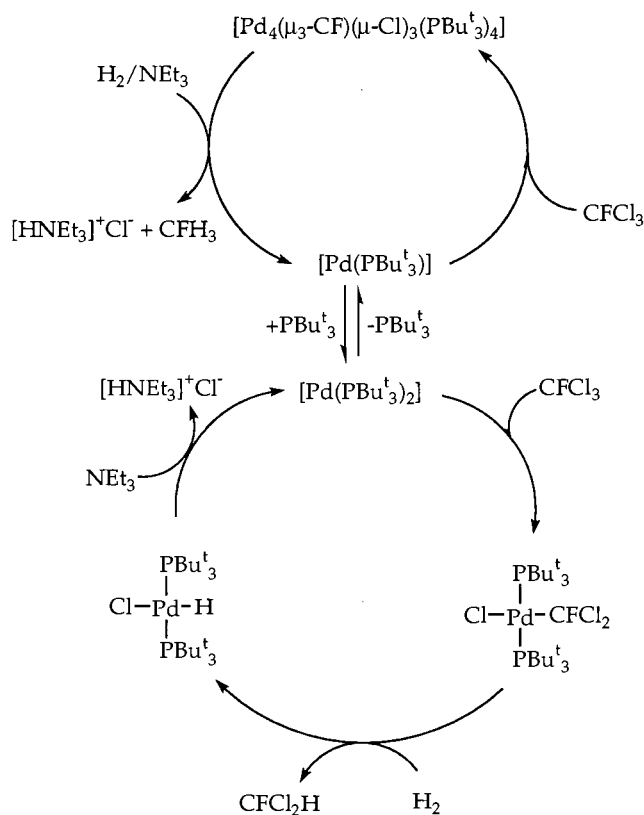
This stoichiometric reaction established that the capping CF group could be converted to CFH_3 with H_2 . However, it was of interest to establish whether this reaction could form the basis of a catalytic cycle. The activation of CFCl_3 (one of the ozone-layer depleting CFCs [44]) in the palladium cluster and its further reaction with H_2 to give CFH_3 has interesting environmental implications. The importance of finding facile routes to convert CFCs (chlorofluorocarbons) to HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons) has been extensively discussed during the last few years [45]. Even though it is still a matter of debate, the HFCs have proved to be possible substitutes for CFCs. Hydrofluorocarbons have some of the physical and chemical properties that have made CFCs so attractive, but due to the absence of chlorine atoms in their structure they do not deplete the ozone layer. Some of the processes used to convert CFCs to the safer HFCs are based on supported palladium catalysts. For example Pd/AlF_3 converts dichlorodifluoromethane to difluoromethane and methane [46].

The hydrogenation process when combined with the cluster forming reaction can be written as shown below:

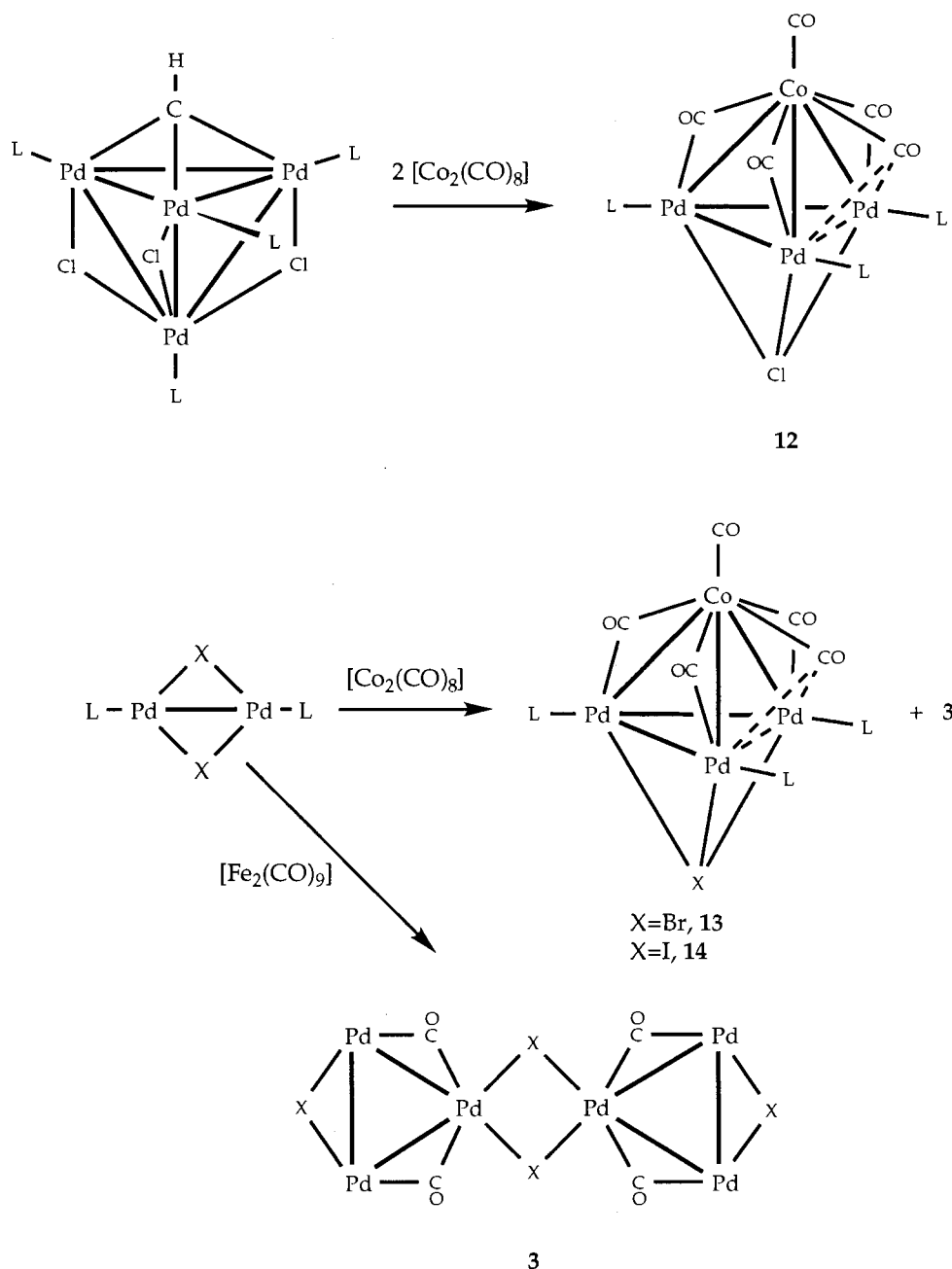


It was important to establish whether it is possible to regenerate the cluster forming reaction from the palladium–phosphine fragments obtained after the hydrogenation. If this is feasible a catalytic cycle to convert CFCl_3 to CFH_3 will have been created.

Although the formation of $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3^t)_4]$ from CFCl_3 and its subsequent hydrogenation provides an illustration of how CFCl_3 may be hydrogenated to CFH_3 on a metal surface, the cluster compound itself is not an effective homogeneous catalyst. When H_2 was bubbled through a solution of $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3^t)_4]$ in toluene in the presence of NEt_3 and with a 50-fold excess of CFCl_3 , the gases produced were identified as CFH_3 and CFCl_2H [17]. $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR data confirmed that the



Scheme 6. Plausible mechanistic cycles for the hydrogenation of CFCl_3 .



Scheme 7. Products of the reactions between $[\text{Pd}_2(\mu\text{-X})(\text{PBu}_3)_2]$ and $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ and $[\text{Co}_2(\text{CO})_8]$.

cluster had fragmented during this reaction. This suggests that the regeneration of the cluster under these reaction conditions is not fast enough and some hydrogenation *side* products are obtained. It appears that the palladium–phosphine fragments generated from the cluster are also responsible for catalysing the hydrogenation of CFCl_3 .

When the hydrogenation reaction was repeated using the mononuclear compound $[\text{Pd}(\text{PBu}_3)_2]$, generated in situ from $[\text{Pd}_2(\text{dba})_3]$ and PBu_3 , with an excess of CFCl_3 (50 to 1 relative to $[\text{Pd}_2(\text{dba})_3]$), the only

hydrogenation product observed was CFCl_2H . Complete conversion of the CFCl_3 to CFCl_2H required 24 h. No traces of CFH_3 or any other gas were detected, suggesting that the cluster $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ plays an essential role in the hydrogenation of CFCl_3 to CFH_3 .

Scheme 6 summarises plausible mechanistic cycles involving the reactions for the mononuclear and tetranuclear palladium compounds. Although in the absence of hydrogen the formation of the tetranuclear cluster with the $\mu_3\text{-CF}$ group proceeds at a sufficient

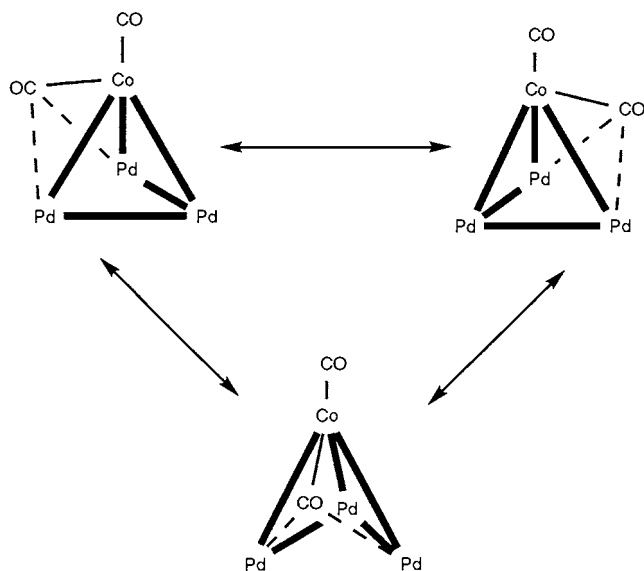


Fig. 1. Hypothetical fluxional process undergone by the CO groups in the palladium-cobalt clusters.

rate to compete with the formation of the simple oxidative addition products, the hydrogenation step proceeds more quickly for the mononuclear product than for the tetranuclear compound leading to the formation of CFCl_2H in addition to CFH_3 . Attempts are currently being made to use variations in the ligands to change the relative rates of the competing cycles and thereby improve the selectivity of the catalytic hydrogenation process.

3.3. Synthesis of palladium-cobalt cluster compounds

Heterometallic cluster compounds have received considerable attention in part because they represent a synthetic challenge but more importantly because of their potential in novel catalytic and stoichiometric reactions [47]. The different possible reactivities of the constituent metals and the possible co-operation between the metal centres make multimetallic systems unique [48].

These precedents encouraged us to study the reactions of the compounds $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ and $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$ ($\text{X} = \text{Br}, \text{I}$) with $[\text{Co}_2(\text{CO})_8]$ [21]. The reactions observed are summarised in Scheme 7.

When $[\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ in toluene is allowed to react with $[\text{Co}_2(\text{CO})_8]$ the new heterometallic cluster $[\text{CoPd}_3(\mu_3\text{-Cl})(\mu\text{-CO})_3(\mu_3\text{-CO})(\text{CO})(\text{PBu}_3)_3]$ (**12**) is obtained. Its molecular structure has been determined by an X-ray structural analysis which showed that the compound obtained has a metal core formed by three palladium atoms and one cobalt atom in what may be described either as a distorted tetrahe-

dral or a butterfly type structure [21]. The presence of five carbonyl ligands around the cobalt (three bridging the Pd-Co bonds, one terminal and one semibridging the Pd-Co-Pd face) is unusual but not unprecedented in cases where there are several bridging CO ligands [49]. This heterometallic cluster has an electron count of 60 which would agree with a tetrahedral structure according to the Polyhedral Skeletal Electron Pair Theory (PSEPT) [40].

Solution IR and ^{31}P -NMR studies have suggested that this cluster undergoes some fluxional process in solution. A rearrangement process involving CO mobility is suspected according to the NMR results. This type of fluxionality has been extensively studied for carbonyl clusters of the Group 8 and 9 metals [50]. A plausible rearrangement process is shown in Fig. 1.

Similar products to $[\text{CoPd}_3(\mu_3\text{-Cl})(\mu\text{-CO})_3(\mu_3\text{-CO})(\text{CO})(\text{PBu}_3)_3]$ were obtained on treating $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$ ($\text{X} = \text{Br}, \text{I}$) in toluene with one equivalent of $[\text{Co}_2(\text{CO})_8]$ [21].

In these reactions, besides the heterometallic clusters, a second product is formed. For the reaction between $[\text{Pd}_2(\mu\text{-Br})_2(\text{PBu}_3)_2]$ and $[\text{Co}_2(\text{CO})_8]$ a second orange product, in addition to $[\text{CoPd}_3(\mu_3\text{-Br})(\mu\text{-CO})_3(\mu_3\text{-CO})(\text{CO})(\text{PBu}_3)_3]$, has been isolated and characterised as $[\text{Pd}_6(\mu\text{-Br})_4(\mu\text{-CO})_4(\text{PBu}_3)_4]$ which is also obtained from the reaction of $[\text{Pd}_2(\mu\text{-Br})_2(\text{PBu}_3)_2]$ with CO (vide supra).

4. Conclusions

The reaction between $[\text{Pd}_2(\text{dba})_3]$ and two equivalents of PBu_3 in the presence of organic halides results in the syntheses of the novel dimers $[\text{Pd}_2(\mu\text{-X})_2(\text{PBu}_3)_2]$ ($\text{X} = \text{Br}$, **1**; I , **2**) and the tetranuclear cluster compounds $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-X})_3(\text{PBu}_3)_4]$ ($\text{R} = \text{H}, \text{F}$ and $\text{X} = \text{Br}, \text{Cl}$). These compounds exhibit interesting reactions and some catalytic activity. The dimers **1** and **2** have proved to be very versatile precursors for a wide variety of reactions. They function as $[\text{Pd}(\text{P-Bu}_3)\text{X}]$ -fragment sources for the synthesis of cluster compounds. This has been exemplified by the synthesis of homometallic clusters $[\text{Pd}_4(\mu\text{-Br})_3(\mu\text{-CO})_2(\text{Bu}^t\text{-PCMe}_2\text{-CH}_2)(\text{PBu}_3)_2]$ and $[\text{Pd}_6(\mu\text{-Br})_4(\mu\text{-CO})_4(\text{PBu}_3)_4]$ and the palladium-cobalt clusters $[\text{CoPd}_3(\mu_3\text{-X})(\mu\text{-CO})_3(\mu_3\text{-CO})(\text{CO})(\text{PBu}_3)_3]$ ($\text{X} = \text{Br}, \text{I}$). The activation of small molecules between the two palladium centres has also been discussed and is an area of increasing interest.

The tetranuclear clusters $[\text{Pd}_4(\mu_3\text{-CR})(\mu\text{-X})_3(\text{PBu}_3)_4]$ represent the first examples of alkylidyne cluster compounds of palladium. Their reactivity has been discussed in this review. Particularly interesting are the reactions that involve the CR capping group. Of spe-

cial relevance is the reaction between $[\text{Pd}_4(\mu_3\text{-CF})(\mu\text{-Cl})_3(\text{PBu}_3)_4]$ and H_2 in which CFH_3 is produced. This seems to be a key step for the catalytic hydrogenation of CFCl_3 to CFH_3 .

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